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catalytic oxidation of acetylene mixed with air on a diaphragm made of active manganese dioxide. A powder of active manganese dioxide was mixed with fibrous asbestos, and the mixture in a damp state was manually pressed into the glass tube of the apparatus, where it was dried.

After escaping from the apparatus, gases were analyzed as follows: traps, filled with silica gel and cooled with liquid oxygen, collected for a definite period of time the carbon dioxide formed as a result of acetylene oxidation. Then, carbon dioxide, gradually heated to 100° C, was blown into traps charged with a solution of barium hydroxide, the excess of which was titrated with hydrochloric acid. The diffusion rate of acetylene was also determined by its capture under similar conditions. Acetylene thus accumulated was blown into ammonia solution of silver nitrate; the precipitate of silver acetylide was filtered off, washed, dissolved in hot nitric acid, and silver was determined according to Volhard.

Determination of Rate and Effective Coefficient of Gas Diffusion Through Diaphragm

One part of the reactor was fed with air containing acetylene in a concentration of from 0.002 to 0.008 milliliters per cubic centimeter, while the other part was filled with pure air. Acetylene which penetrated through the diaphragm was carried away with pure air, and its quantity was determined by the method described. The amount of acetylene diffused per second corresponds to the diffusion rate.

Simultaneously, the quantity of acetylene was determined in the air-gas mixture leaving the first reactor part. Results of determinations were in agreement with total amount of acetylene at low temperatures. Up to 70-80° C the quantities of acetylene check, indicating the absence of any chemical process, whereas the rate of diffusion does not depend on temperature.

Here are the results of one series of experiments. Thickness of the diaphragm $\rho = 1.34$ cm, its cross section $\rho = 4.52$ sq cm, acetylene concentration in the initial mixture $C_0 = 0.008 \frac{\text{ml C}_2\text{H}_2}{\text{cu cm}}$, the rate of flow of pure air $v = 10 \frac{\text{ml}}{\text{sec}}$. The rate of diffusion up to 70° C: $W_{\text{dif}} = 2.6 \cdot 10^{-3} \frac{\text{ml C}_2\text{H}_2}{\text{sec}}$

The effective coefficient of diffusion D^* may be calculated from data on the rate of diffusion. This coefficient is a magnitude introduced into numerous equations of macrokinetics but it never has been determined experimentally.

According to the Fick equation, $D^* = \frac{W_{\text{dif}} \cdot \rho}{(C_0 C) S}$

Because $C = \frac{W_{\text{dif}}}{v}$, e.g., in our case $C = 2.6 \cdot 10^{-4} \frac{\text{ml C}_2\text{H}_2}{\text{cu cm}}$, hence $D^* = \frac{2.6 \cdot 10^{-3} \cdot 1.34}{4.52(0.0080 - 0.00026)} = 0.10 \frac{\text{sq cm}}{\text{sec}}$

This example corresponds to the most porous of all tested diaphragms. In the case of greater density of the diaphragm, the value of D^* decreased. The lowest value of D^* for the diaphragm made of MnO_2 and asbestos was $0.01 \frac{\text{sq cm}}{\text{sec}}$

Investigation of Kinetics of the Process

The experimental procedure was the same as in the investigation of the diffusion rate. Experiments have been conducted with various diaphragms at acetylene concentrations of 0.2, 0.4, 0.6, and $0.8 \frac{\text{ml}}{\text{cu cm}}$ at temperatures from

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room temperature to 450° C. All series of experiments give analogous results. Oxidation of acetylene begins above 80° C and is quite noticeable at 110° C judging from the amount of acetylene penetrating through the diaphragm. This amount decreases and at 170° C there is no acetylene at all behind the diaphragm. Obviously, all acetylene is oxidized during its diffusion through the diaphragm.

Thus, the process on porous catalysts, as envisaged by contemporary theories of macrokinetics, is illustrated directly by experiments described. It is demonstrated that only in the temperature range of 80-110° C is there almost no decrease in concentration of acetylene in the layer despite the oxidation process, a state which corresponds to conditions of the internal kinetic region. Above this temperature the concentration in the layer decreases, which is equivalent according to Ya. B. Zel'dovich [1] to a decrease of the depth of the operating layer e.g., the reaction enters the transitional or inner diffusion region.

Experimental results permit quantitative treatment on the basis of the Fick equation: $\frac{dx}{dt} = -D \frac{dc}{d\rho}$, where $\frac{dx}{dt}$ is the rate of gas penetration through the outer surface of the diaphragm and $\frac{dc}{d\rho}$ is the gradient of concentration in the frontal surface layer. The value of $\frac{dx}{dt}$ obviously is equal to the sum of acetylene quantities reacted in the diaphragm ($W_{chem.}$) and penetrated beyond the layer ($W_{dif.}$). Therefore, $W_{chem.} + W_{dif.} = -D \frac{dc}{d\rho}$. This equation permits obtaining some essential data on the process. Let us demonstrate this possibility by calculating the apparent order of the reaction in the inner diffusion region (Zel'dovich's region).

It is obvious that $W_{dif.} = 0$ at 170° C. Therefore, above this temperature the last equation will assume the form: $W_{chem.} = -D \frac{dc}{d\rho}$, but $W_{chem.} = kC^n$, from which $kC^n = -D \frac{dc}{d\rho}$ (3)

Separating the variables, we integrate in the limits from C_0 to C and from 0 to ρ

$$C^{1-n} - C_0^{1-n} = -\frac{(1-n)k}{D \cdot S} \rho, \quad (4)$$

where ρ is the distance of a given layer from the frontal surface of the diaphragm, C_0 is the concentration at this outer surface, and C is the concentration at distance ρ from it. Let us apply this equation to conditions existing in the layer at 170° C. At this temperature C is equal to 0 at the rear side of the diaphragm, e.g., when $\rho = \rho_0$:

$$C_0^{1-n} = \frac{(1-n)k}{D \cdot S} \rho_0$$

or substituting k by $\frac{W_0}{C_0^n}$, where W_0 is the reaction rate at 170° C,

$$n = 1 - \frac{C_0 D \cdot S}{W_0 \rho_0} \quad (5)$$

Let us introduce values from the experiment:

$$n = 1 - \frac{0.008 \cdot 0.1 \cdot 4.52}{7 \cdot 10^{-3} \cdot 1.34} = 0.62$$

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The knowledge of values of D^* and n makes possible the calculation of the distribution of acetylene concentrations across the thickness of the diaphragm at all temperatures above 170°C using the equation (3).

Direct determination of the reaction order for a definite kinetic region established by operating at low reaction rates is difficult, but according to Y. B. Zel'dovich, the relation between the reaction order in the inner kinetic region m and the reaction order for the inner diffusion region n may be expressed by the equation $n = \frac{m+1}{2}$. In our case $n = 0.62$, then $m = 0.24$. Graphical comparison with experimental data showed a good agreement.

The diaphragm method may be used also for calculating the distribution of concentrations in the catalyst at low temperatures. In cases when the catalyst has nonuniform activity, this factor may be detected and studied by the diaphragm method. Finally, the diaphragm method makes it possible to clarify the influence of conditions of catalyst formation and of external diffusion resistances (layer of inert gas) on catalyst activity. For example, in order to carry out investigations of this type different conditions were created on both sides of the diaphragm during formation of the catalyst under conditions corresponding to the process near the kinetic region. The reaction mixture was fed to one side and the other side was filled with an inert gas. On changing the flow direction, the nonuniformity of activity across the layer affects the catalyst action, because either the more active part of the diaphragm or the less active will alternately be in the region of high concentrations and this factor will cause differences in the reaction rates.

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